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An Ab Initio Study of the Geometry and Rotational Barrier of 4-Phenylimidazole

by

Peter V. Maye and Carol A. Venanzi

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An Ab Initio Study of the Geometry and Rotational Barrier of 4-Phenylimidazole

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Abstract

The molecular design of several synthetic artificial enzymes, which mimic the action of the serine protease alpha-chymotrypsin, incorporates the phenylimidazole molecular fragment to play the role of the His-57 residue in the native enzyme active site. Study of these artificial enzymes by molecular modelling techniques requires accurate torsional force field parameters for the phenylimidazole inter-ring bond. This, in turn, requires accurate characterization of the barrier to rotation around this bond. Previous semi-empirical calculations of this rotational barrier have neglected geometry optimization of the molecule at the points along the rotational pathway. The 4-phenylimidazole rotational barrier (5.16 kcal/mol) presented here was obtained by full ab initio geometry optimization at the 3-21G level at each of the points along the rotational pathway.

Keywords:
Molecular orbital theory, Phenylimidazole, Rotational barrier, Artificial enzymes.

I. INTRODUCTION

The phenylimidazole molecular fragment plays a primary role in the functional architecture of biologically active molecules such as novel histamine H_2-receptor antagonists[1], cardiotropic agents[2], and several types of artificial enzymes[3-6]. A current interest in this laboratory is the study of the structural basis of the activity of artificial enzyme models via molecular mechanics and molecular dynamics modeling techniques[7-11]. In order to obtain meaningful results from such calculations, high quality force fields are needed in order to compute realistic molecular conformations and accurate energies. The basic motivation for the work presented here is the calculation of the rotational energy barrier for 4-phenylimidazole. This information will be used to derive an accurate rotational force constant for use in subsequent molecular modelling studies of enzyme models incorporating this molecular fragment.

A previous theoretical study[12] of the relationship between inter-ring twist and the conformational energies of the isomers of phenylimidazole used extended Hückel, CNDO/2, and PCILO methods to calculate conformational energies for rigid rotations of 0°, 30°, 60°, 90°, 120°, 150° and 180° of the inter-ring torsional angle.

The phenylimidazole geometry used for the rigid rotations in that calculation was constructed from an X-ray structure of imidazole combined with a benzene fragment of standard geometry. The geometry was not optmized at each new torsional angle.

A more recent study[13] used the MNDO method to optimize the geometry of 4-phenylimidazole in the planar conformation. This geometry was then used to calculate the barrier for rigid rotations of 0^{o}, 30^{o}, 60^{o}, 90^{o}, 120^{o}, 150^{o} and 180^{o} inter-ring twist using the CNDO/2 method.

Since these earlier studies gave different results for the barrier height, it seemed important to determine the barrier using a high-quality ab initio basis set. The work presented here gives the fully-optimized geometry of 4-phenylimidazole in seven conformations (with 0^{o}, 30^{o}, 60^{o}, 90^{o}, 120^{o}, 150^{o} and 180^{o} of inter-ring twist) in the 3-21G basis set. Similar calculations are currently proceeding for the other (1-, 2- and 5-) isomers of phenylimidazole and will be reported in a future publication.

II. METHODS

The initial coordinates for the structural optimization of 4-phenylimidazole were based on standard bond length and bond angle geometry. The CC bond lengths were taken as 1.390 Å, the CN bond

Å = Angstrom unit

lengths as 1.360 Å, the CH bond lengths as 1.100 Å, the NH bond length as 1.000 Å and the CC inter-ring bond length as 1.480 Å. The initial bond angles were assigned by assuming an equiangular hexagonal geometry for the phenyl ring and an equiangular pentagon for the imidazole ring. Both rings were initially assumed to be perfectly planar. The initial coordinates were subjected to molecular mechanics refinement using the AMBER program[14]. These coordinates were then subjected to a Berny gradient optimization in the 3-21G basis set using the Gaussian 86 [15] ab initio quantum chemistry program. The initial geometry optimization proceeded in two steps. First, with the inter-ring twist angle ($C_{11}C_6C_4N_3$, see Figure 1) constrained to 0°, the geometry of the C_4C_6 bond and the hydrogen atoms ortho to these carbon atoms (on C_5, C_7 and C_{11}) were optimized. Then, with the C_4C_6 twist angle still constrained to 0°, a full optimization was carried out. Full optimization was repeated with the inter-ring twist angle constrained to 30°, 60°, 90°, 120°, 150° and 180°; each optimization used the phenyl and imidazole ring geometries of the fully-optimized planar structure as the starting point.

III. RESULTS AND DISCUSSION

The energies of the optimized structures relative to the optimized structure with the 0° twist angle, are found at the bottom

of Table I. The geometry of the optimized structure with perpendicular phenyl and imidazole rings is the highest energy structure on the rotational pathway, yielding a rotational barrier of 5.16 kcal/mol relative to the fully planar conformations at 0^{o} and 180^{o}. The magnitude of the barrier appears reasonable considering experimental barriers to rotation around partial double bonds in aromatic molecules such as styrene[16] (3.3 kcal/mol) and benzaldehyde[17] (4.6 kcal/mol). The present work agrees with previous calculations[12,13] in finding the planar conformation to be the most stable. However, the CNDO/2 calculations using the MNDO-optimized planar geometry[13] predicted a rotational barrier of only 1.4 kcal/mol and a very slight rise in the energy (less than 0.5 kcal/mol) between 0^{o} and 45^{o}. In the present calculation, the energy rises more sharply in this region and continues to rise even more steeply beyond 45^{o} to reach the maximum of 5.16 kcal/mol at 90^{o}.

The 3-21G barrier of 5.16 kcal/mol is roughly comparable to the PCILO value[12] of 6.65 kcal/mol. Some error, however, arises in the latter calculation due to neglect of geometry optimization at the points along the rotational pathway. For example, the PCILO calculations gave an asymmetry in the rotational barrier around the 90^{o} data point (see Table I, bottom row); there is a difference of approximately 1.4 kcal/mol in the energies of the 60^{o} and 120^{o} conformations. However, these conformations are symmetry-related and should be of equal energy. In contrast to the PCILO results, the

results presented in Table I give an essentially symmetrical rotational barrier around the 90° twist conformation.

Our ab initio results give a rotational barrier for 4-phenylimidazole which is conderably higher than the values obtained with rigid rotations using standard geometry and the CNDO/2 or extended Hückel methods (0.02 or 0.16 kcal/mol, respectively)[12], or for rigid rotations using MNDO-optimized planar geometry and the CNDO/2 method (1.4 kcal/mol)[13]. Therefore, our results suggest that the preference of 4-phenylimidazole for a planar conformation is considerably greater than indicated by the CNDO/2 results.

It should be noted that, in general, ab initio rotational barriers have not been shown to be more accurate than those calculated with semi-empirical techniques. However, the large rotational barrier calculated here seem more reasonable than the CNDO/2 results considering that rotation in 4-phenylimidazole involves breaking a partial double bond.

Comparison of the optimized geometries from our calculations at 0° (Table I) with the MNDO-optimized planar geometry reported by Donetti and coworkers[13] shows that the 3-21G values for the imidazole heavy atom-heavy atom bond lengths tend to be shorter than the corresponding MNDO bond lengths. The differences range from 0.010 Å for C_4C_6 to 0.045 Å for C_4C_5. The N_1H_1 bond lengths agree, while the C_2H_2 and the C_5H_5 bond lengths are 0.02 Å larger than the MNDO calculation. The internal imidazole bond angles in the two

calculations are quite similar, whereas the external angles differ by 0.2 Å for $H_1N_1C_2$ to 1.1 Å for $H_5C_5C_4$. The $C_5C_4C_6$ angle is 130° in both calculations.

The two calculations differ by 2°-3° in the values for the $H_{11}C_{11}C_6$, $H_7C_7C_6$, and $C_7C_6C_4$ angles, but since the rest of the benzene ring was kept rigid in the Donetti calculation[13], the 3-21G results for these geometries are likely more accurate.

Comparison of the optimized geometries of the 0° and 90° conformations obtained in our ab initio calculations shows that the largest difference in bond angle for these conformers is a 2.4° increase in the $C_5C_4C_6$ bond angle on the imidazole side of the inter-ring linkage in the 0° conformer relative to the 90° conformer. There is a similar trend in the slightly smaller (1.5°) increase in the $C_4C_6C_7$ bond angle of the 0° conformer relative to the 90° conformer. These changes could serve to slightly separate the ortho substituents in the 0° (or 180°) conformer.

The largest bond length difference between the 0° and 90° conformers is found in the C_4C_6 bond linking the two rings. This increases from 1.466 Å in the 0° confomer to 1.478 Å in the 90° conformer. The increase in bond length upon rotation is presumably due to loss of electron conjugation between the rings.

Table I also contains calculated values for the $C_4C_6C_9$ angle and the deviations of the phenyl and imidazole rings from planarity. Examination of these quantities shows that the deviations of $C_4C_6C_9$

from linearity and of the phenyl and benzene rings from planarity are small.

Bond lengths obtained for individual benzene and imidazole molecules calculated in the 3-21G(*) and 6-31G* basis sets are also available for comparison with the bond lengths of 4-phenylimidazole[18]. The largest observable differences in the bond lengths of phenylimidazole relative to the component ring molecules occur in the 0^{o} conformer in the ring bonds flanking the C_4C_6 inter-ring bond. The C_6C_7 and C_6C_{11} bonds of the phenyl portion and the C_4C_5 imidazole bond are each lengthened about 0.005 Å (in the planar conformation) relative to the values in benzene and imidazole. The same bonds in the 90^{o} conformer deviate only by about 0.0025 Å for C_6C_7 and C_6C_{11}, and by less than 0.001 Å for C_4C_5 from the corresponding benzene and imidazole bond lengths.

Comparison of our calculated geometries may be made with experimental geometries for benzene and imidazole. The calculated phenyl ring bond lengths are on the order of 0.01 Å shorter than the CC bond length found for benzene (1.396 Å)[20]. The calculated imidazole ring bond lengths in 4-phenylimidazole at $C_{11}C_6C_4N_3$ equal to 0^{o} differ from the neutron diffraction imidazole bond lengths (1.347 A for N_1C_2, 1.322 Å for C_2N_3, 1.375 Å for N_3C_4, 1.368 Å for C_4C_5 and 1.369 Å for C_5N_1)[21] by a maximum value of 0.024 Å for C_2N_3. The experimental imidazole bond angles (111.92^{o} for $N_1C_2N_3$, 105.14^{o} for $C_2N_3C_4$, 109.80^{o} for $N_3C_4C_5$, 106.02^{o} for $C_4C_5N_1$ and 107.11^{o} for

$C_5N_1C_2$)[21] and the calculated values at $C_{11}C_6C_4N_3$ equal to 0° differ by a maximum of 1.74° for $C_2N_3C_4$.

Mean absolute errors for geometric parameters involving heavy atoms have been calculated for the 3-21G basis set[19]. These are on the order of several hundredths of an Angstrom for bond lengths (0.033 Å for single bonds from 126 comparisons, 0.019 Å for double bonds, from 60 comparisons) and on the order of a degree for bond angles (1.0 degree, from 70 comparisons). Thus our reported geometries cannot be considered accurate to the number of figures reported. Also, our calculations were carried out with a relatively small basis set and without electron correlation.

In summary, the 3-21G results presented here indicate that 4-phenylimidazole has a significant barrier to rotation (5.16 kcal/mole). The effect of this barrier on the orientation of the imidazole functionality with respect to the other catalytic components of an artificial enzyme binding site[3,4] and with respect to the substrate will be examined in future molecular mechanics and molecular dynamics calculations in this laboratory.

Finally, as mentioned in the Introduction, similar ab initio calculations are proceeding in this laboratory to determine the rotational barriers and geometries of the 1-, 2- and 5-phenylimidazole isomers. Information from these calculations will be used, via molecular modeling, to determine how the orientation of the phenylimidazole portion of the molecular architecture of the mimic is affected by different isomeric substitutions.

ACKNOWLEGEMENT

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TABLE I. Energy and Geometry of 4-Phenylimidazole[a]

Geometric Parameter	$C_{11}C_6C_4N_3$ Torsional Angle						
	0°	30°	60°	90°	120°	150°	180°
$r(N_1C_2)$	1.366	1.366	1.366	1.366	1.366	1.366	1.366
$r(C_2N_3)$	1.298	1.299	1.300	1.300	1.300	1.299	1.298
$r(N_3C_4)$	1.395	1.395	1.396	1.397	1.396	1.395	1.395
$r(C_4C_5)$	1.358	1.358	1.355	1.353	1.355	1.357	1.358
$r(C_5N_1)$	1.383	1.383	1.384	1.384	1.383	1.383	1.383
$r(C_4C_6)$	1.466	1.466	1.471	1.478	1.471	1.466	1.466
$r(C_6C_7)$	1.390	1.389	1.388	1.387	1.390	1.390	1.390
$r(C_7C_8)$	1.382	1.383	1.385	1.384	1.382	1.382	1.382
$r(C_8C_9)$	1.384	1.384	1.383	1.384	1.386	1.385	1.384
$r(C_9C_{10})$	1.384	1.385	1.386	1.384	1.383	1.384	1.384
$r(C_{10}C_{11})$	1.382	1.382	1.382	1.384	1.385	1.383	1.382
$r(C_{11}C_6)$	1.390	1.390	1.389	1.388	1.388	1.389	1.391
$r(N_1H_1)$	0.994	0.994	0.994	0.994	0.994	0.994	0.994
$r(C_2H_2)$	1.063	1.064	1.064	1.064	1.064	1.064	1.064
$r(C_5H_5)$	1.063	1.063	1.063	1.063	1.063	1.063	1.063
$r(C_7H_7)$	1.072	1.072	1.072	1.072	1.071	1.070	1.070
$r(C_8H_8)$	1.072	1.072	1.072	1.072	1.072	1.072	1.072

TABLE I. (Continued)

$r(C_9H_9)$	1.072	1.072	1.072	1.072	1.072	1.072	1.072
$r(C_{10}H_{10})$	1.072	1.072	1.072	1.072	1.072	1.072	1.072
$r(C_{11}H_{11})$	1.070	1.070	1.071	1.072	1.072	1.072	1.072
L = ANGLE SYMBOL							
$<(N_1C_2N_3)$	110.96	111.05	111.13	111.18	111.13	111.02	110.96
$<(C_2N_3C_4)$	106.88	106.72	106.51	106.40	106.51	106.73	106.90
$<(N_3C_4C_5)$	108.84	108.97	109.13	109.22	109.13	108.98	108.83
$<(C_4C_5N_1)$	106.21	106.19	106.19	106.24	106.20	106.17	106.21
$<(C_5N_1C_2)$	107.10	107.05	107.01	106.95	107.01	107.08	107.10
$<(C_5C_4C_6)$	130.02	129.32	128.30	127.65	128.04	129.31	130.05
$<(C_4C_6C_7)$	121.94	121.52	121.02	120.44	119.79	119.40	119.18
$<(C_6C_7C_8)$	120.55	120.48	120.47	120.45	120.40	120.37	120.44
$<(C_7C_8C_9)$	120.24	120.18	120.06	120.09	120.19	120.34	120.39
$<(C_8C_9C_{10})$	119.51	119.59	119.73	119.78	119.72	119.58	119.49
$<(C_9C_{10}C_{11})$	120.37	120.32	120.20	120.05	120.10	120.18	120.23
$<(C_{10}C_{11}C_6)$	120.44	120.37	120.38	120.49	120.46	120.49	120.57
$<(C_{11}C_6C_7)$	118.89	119.03	119.12	119.14	119.13	119.04	118.88
$<(H_1N_1C_5)$	126.10	126.15	126.24	126.28	126.22	126.16	126.11
$<(H_2C_2N_1)$	122.91	122.89	122.85	122.83	122.83	122.88	122.92
$<(H_5C_5C_4)$	131.63	131.29	130.93	130.84	130.93	131.29	131.61
$<(H_7C_7C_6)$	120.14	119.78	119.37	119.30	119.04	118.71	118.49
$<(H_8C_8C_9)$	120.06	120.07	120.08	120.07	119.99	120.01	120.01
$<(H_9C_9C_{10})$	120.32	120.22	120.13	120.11	120.17	120.17	120.18

TABLE I. (Continued)

$<(H_{10}C_{10}C_{11})$	119.61	119.68	119.79	119.85	119.81	119.75	119.71
$<(H_{11}C_{11}C_{10})$	121.08	120.92	120.54	120.22	120.14	119.72	119.32
$<(C_4C_6C_9)$	178.65	178.98	178.67	179.80	177.09	177.90	178.65
Phenyl Ring Planarity[b]	0.01	0.67	1.16	0.11	0.23	0.34	0.01
Imidazole Ring Planarity[c]	0.00	0.69	0.97	0.00	0.95	0.68	0.02
Relative Energy[d]	0.00	0.71	3.22	5.16	3.20	0.71	0.00
Relative Energy[e,f]	0.000	1.996	5.602	6.647	4.231	1.043	0.000

a. 3-21G basis set. Energy in kcal/mol, distances in Å, angles in degrees.

b. Average deviation from planarity, in degrees, of the 6 dihedral angles of the phenyl ring involving heavy atoms.

c. Average deviation from planarity, in degrees, of the 5 dihedral angles of the imidazole ring involving heavy atoms.

d. Relative to the total energy at 0° and 180°, -283,523.13 kcal/mol.

e. PCILO results, Ref. 12; relative to the total energy at 0°, 58,764.124 kcal/mol.

f. The CNDO/2 and extended Hückel results are only presented in graphical form in Figures 2 and 3 of Ref 12 and Figure 2 of Ref. 13. See text for comparison of results.

Legend to Figure.

Figure 1. Schematic diagram of the structure of 4-phenyl-imidazole.

H9
C9
H8
C8
H10
C10
C7
C11
H7
H11
C6
C4
H5
C5
N3
N1
C2
H1
H2

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